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Hayward R. Baker and Robert N. Bolster

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Water condensation						
Moisture displacement						
Electronics coatings						
Surface conductivity						
Water repellency						

CONTENTS

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PROBLEM STATUS

This is an interim report; work on this subject is continuing.

AUTHORIZATION

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THE PREVENTION OF SURFACE ELECTRICAL LEAKAGE
IN THE PRESENCE OF MOISTURE

INTRODUCTION

In spite of the many recent improvements in insulating materials and protective coatings, surface electrical leakage is still a frequent cause of trouble in electrical and electronic equipment. This results from the increasing complexity and sensitivity of the equipment and from the trend toward miniaturization and compactness. The problem is, of course, most severe in marine environments, where salt particles can be deposited on the insulator surfaces, and with airborne equipment, which is often exposed to temperature and humidity conditions that result in moisture condensation on insulator surfaces. The resulting surface electrical leakage may change the characteristics of high-impedance circuits, induce flashover on high-voltage insulators, ground power circuits, or short-out control circuits.

Previous work at NRL on the displacement of water from solid surfaces (1,2) led to the development of the butanol-based water-displacing fluid used in the salvage of flooded or contaminated electrical and electronic equipment (3-7). Although this material is effective in drying equipment, restoring insulation resistance, and inhibiting corrosion, its effects on the insulation resistance of equipment upon subsequent exposure to moisture were not quantitatively known. Numerous commercial water-displacing products, most of them nonvolatile organic liquids containing surface-active additives, were also being used by naval activities without knowledge of their effects on insulation resistance.

Therefore, this investigation was designed to study the surface conductivity of dielectrics under conditions permitting moisture condensation and to determine the effects of surface constitution, water-displacing treatments, and coatings.

An early study of the effects of relative humidity on the surface resistivity of dielectrics was done by Curtis (8) before World War I. It was already known that a thin film of water, together with dissolved salts, was responsible for the conductivity and that easy wettability of the surface favored loss of resistivity with increasing humidity. Field (9,10) studied the changes in insulator surface resistivities with time at 100% relative humidity and recoveries of resistivity upon drying. The resistivities of most dry insulator surfaces were found to be in the range of 10^6 to 10^{10} megohms. Upon exposure to air at 100% relative humidity, the resistivities of the most hydrophobic surfaces decreased by two or three orders of ten, and those of hydrophilic surfaces decreased by five to seven orders. Still poorer were some of the obsolete materials studied by Curtis, probably because of soluble or even hygroscopic salts in them, as he noted. Field also measured the recovery of resistivity when samples were transferred from saturated to dry air. The recovery was slowest for porous materials, those with large volume absorption of water, and hydrophilic materials.

Only on polystyrene did Field condense bulk water by cooling the surfaces slightly below the dew point. He found the ultimate surface resistivity under this condition to be about 10^5 megohms, one order of ten lower than it was at 100% relative humidity without condensation. The recovery of surface resistivity after the sample was placed in dry air required about ten times as long due to the greater volume of water on the surface.

The condensation of bulk water on electrical insulation is obviously more detrimental than the effects of high humidity alone, but almost no data were available on the effect of bulk water on the surface resistivities of various dielectrics or on the effectiveness of

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water-displacing agents or protective coatings. Smail, Brooksbank, and Thornton observed the resistivity of glass in an atmosphere of constant temperature and humidity as the temperature of the surface was decreased (11). They found that the surface resistivity decreased logarithmically as the surface temperature was lowered. After the dew point was passed, however, there was a significant rise in the resistivity, followed again by a decrease. They attributed this effect to the growth of the adsorbed monolayer of water to a thickness such that it became unstable and contracted into droplets with a smaller total surface area. This explanation is not always applicable since it neglects the energy necessary to transform the area between the droplets from solid/liquid interface into solid/vapor interface. Young (12) pointed out the equilibrium conditions governing the contact angle of a drop of liquid on a solid surface. The cosine of the contact angle θ is determined by the three surface tensions, which are numerically equivalent to surface free energies:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}},$$

where S = solid, V = vapor, and L = liquid. With a high-energy surface, such as clean glass, γ_{SV} is equal to or greater than $\gamma_{SL} + \gamma_{LV}$, and the contact angle is zero. The liquid wets the surface, and the film will simply become thicker as water condenses and will then flow under the influence of gravity. In the experiments of Smail et al., the glass surfaces undoubtedly adsorbed contaminants from the atmosphere (almost unavoidable) which would decrease γ_{SV}, making $\cos \theta$ less than 1. The water film would then break up as they observed and would form droplets of the appropriate contact angles.

Film and drop condensation on metal surfaces have been studied in relation to their effect on the rate of heat transfer in steam condensers. Some early investigators were misled, by slight surface contamination, to the conclusion that clean metal surfaces induced drop condensation, which improves the rate of heat transfer. Advances in surface chemistry led to an understanding of the adsorption of amphipathic (polar) organic compounds on metal surfaces and the resulting effect on their wettability. Emmons (13) related this knowledge to the mechanism of drop condensation on metals. He employed the spreading coefficient as a criterion for film vs drop condensation. The spreading coefficient, originated by Cooper and Nuttall (14), is closely related to Young's equation and is given by

$$S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}).$$

When S is greater than zero, the liquid spreads, the contact angle is zero, and film condensation occurs. When S is less than or equal to zero, spreading does not occur, and condensation forms drops with finite contact angles.

In describing the wettability of solid surfaces, the concept of critical surface tension developed by Zisman and coworkers (15) is most useful. All surfaces having a γ_c above the surface tension of water will be wet by it, and all those having a γ_c below that value will not be wet. The lower the value of γ_c, the greater the contact angle will be.

To minimize the electrical leakage through the moisture on an insulator surface, the moisture must be made to retract into drops covering a minimum area. This requires an insulator surface with a low γ_c, i.e., a low-energy surface. Since the constitution of the surface affects its surface energy, materials can be selected to obtain the desired properties. Fluorocarbons, hydrocarbons, and silicones generally have low-energy surfaces; polymers with oxygen or nitrogen atoms exposed are intermediate, and glass and ceramics have high-energy surfaces. Bulk electrical and mechanical properties of insulating materials must also be considered, of course, and these factors may require the use of materials without optimum surface properties.

Since low-energy surfaces have less attraction for water molecules than high-energy surfaces, one might surmise that condensation would not occur at the dew point, but rather only at some degree of supersaturation. This is indeed true, and the expected degree of supercooling can be calculated from the Volmer-Becker-Doring equation (16) which includes the contact angle in its terms. Twomey (17) found good experimental confirmation with surfaces producing contact angles up to 90°. Koutsky, Walton, and Baer (18) observed supercooling of 11° and 8°C with Teflon (poly(tetrafluoroethylene)) and benzophenone, respectively. These supercoolings are considerable, even though less than those predicted. In practice such supercooling would be very difficult to achieve, since the surface must be smooth, free of embedded high-energy particles or regions, and free of deposited or adsorbed contaminants. Even so, for a given intermediate degree of supercooling, the number of nucleation sites should be smaller on a low-energy surface than on one which is almost wet by water. The number of droplets per unit of area, the fraction of the surface covered by bulk water, and the surface conductivity should all be less.

EXPERIMENTAL PROCEDURES

Resistivity Measurements

The apparatus used for the measurement of surface resistivity was similar to that used by Smail, Brooksbank, and Thornton (11) in that the atmosphere surrounding the sample was maintained at a constant temperature and humidity while the sample was cooled below the dew point. The tubular insulator samples, similar to those used by Williams and Herrmann (19), were 1/2 in. O.D., 3/8 in. I.D., and 3 in. long. The electrodes, which were placed 1 in. apart, were bands of nickel clamped tightly around the specimen. Silver must be avoided as an electrode material because of its ability to migrate across insulator surfaces under a dc potential (19). The cylindrical geometry eliminated edge effects, and samples of most common insulating materials were available as tubing of this size.

The surface resistivity was calculated by multiplying the measured resistance between the electrodes by the ratio of the electrode length (circumference of the tube) to their separation. In this case, the ratio was 1.57. A brass tube, 3/8 in. O.D. in the center and 1/4 in. at the ends, fit snugly into the specimen tubes. Water from a constant-temperature bath was pumped through this tube to control the temperature of the specimen. Teflon washers 1 in. in diameter were placed over the ends of the brass tube and pushed up against the ends of the sample to guard it against contamination. The test chamber consisted of a 12-in. cylindrical glass jar with a polystyrene cover. The air, circulated by a small blower, was maintained at 26°C by proportionally controlled electric heaters and stabilized at 93% relative humidity by dishes of saturated monobasic ammonium phosphate solution. Since there was a lag in the response as moisture was removed from the air by condensation, a hygrometer-controller was interposed in the chamber heater circuit to select either an air heater or a heater under one of the dishes of ammonium phosphate solution. This increased the rate of evaporation sufficiently to maintain the relative humidity at 93% under dynamic conditions. The dew point in the chamber was about 24.8°C. Water at 20°C was pumped through the specimen assembly, producing a maximum possible supercooling of 4.8°C. The actual supercooling was slightly less, depending on the thermal conductivity of the sample tube wall.

A battery was used to apply a potential of 100 V between the electrodes, and the resulting current was measured with a Keithley 610A electrometer. To prevent interference from exterior electrical fields, connections were made with coaxial cables with grounded shields, and the sample and electrodes were enclosed with grounded copper screen. The brass tube inside the samples was also grounded to serve as a guard electrode. This eliminated the effect of conductivity along the interior of the sample tube and

reduced the effect of volume conductivity. The resistance of the guard circuit was greater than 10^8 megohms under operating conditions. Surface resistivity could be determined up to 10^9 megohms and could be discriminated from infinite resistivity to about 10^{10} meghoms.

Samples of various polymers and composites used as insulators were obtained in tubular form and cut into 3-in. lengths. They were cleaned, usually by washing them in an aqueous detergent solution, rinsed and soaked in water, rinsed in distilled water, oven dried, and stored in a desiccator. The glass and quartz samples were cleaned in a sulfuric-nitric acid bath, then rinsed and dried in a similar manner. None of the surfaces were abraded or polished. The polymer surfaces were therefore in a natural, or slightly oxidized, rather than pristine condition. Coatings were applied by dipping whenever possible, or by spraying or brushing. Commercial coatings were dried or cured according to the manufacturers' instructions.

The sample assembly was placed in the chamber with its axis horizontal, supported by the cooling water tubing, with battery and electrometer connections made to the electrode clamps and the brass tube grounded. The sample was maintained slightly above the chamber temperature until the temperature and humidity of the air stabilized at the proper values. The cooling water circulating pump was then started, and the current passing across the sample surface was recorded continuously as condensation formed for at least 3 hours. The minimum resistivity was the lowest value observed, exclusive of momentary spikes in the recording, during the 3-hour test period. The steady-state value was determined by the asymptote to the resistivity curve or its extrapolation. In many cases where the resistivity was still decreasing at the end of 3 hours, the run was extended to improve the accuracy of this determination. A binocular microscope (30 and 45X) was mounted above the chamber so that the condensation and coalescence could be observed through a viewing window. An angle graticule in one ocular facilitated making rough measurements of the contact angles of droplets.

Water Displacement

The effect of various water-displacing agents on the resistivity of wet surfaces was determined with the same sample assembly and electrical arrangement as for the condensation tests. The sample was exposed to the room air rather than placed in the chamber. The surface was wet with distilled water, and the decrease in conductivity was recorded as the displacing agent was applied and allowed to dry. The sample tube was sprayed from both sides with enough of the agent to cause dripping from the sample. Experimental displacing agents were also evaluated on steel panels. A panel, after surface cleaning by abrasion, was placed in a dish with enough water to cover the panel to a depth of 1 mm. The rapidity, extent, and completeness of displacement were observed after the application of 4 drops of the agent. After the solvent evaporated, the coating formed was examined for continuity and uniformity.

Contact Noise

The effect of coatings on contact resistance was evaluated on typical components: a molded composition potentiometer (with case removed), a wire-wound rheostat, round and flat pin multiple connectors, a 42-contact circuit board connector, a 4PDT wafer switch, and a leaf switch with a pair of DPDT contacts. All switch and connector contacts were wired in series so that noise or open contacts in any of them could be detected. The test circuit imposed an open-circuit potential of 1.5 V dc, and the closed-circuit current was limited by a resistor to 1 mA. As the coated component under test was operated, the potential across the resistor was monitored with an oscilloscope and a voltmeter to detect noise or a lack of contact.

RESULTS AND DISCUSSION

Condensate Formation

Within seconds after the flow of cooling water through the sample tubes was begun, droplets of condensate could be seen on their surfaces with the microscope. Differences between high-energy and low-energy surfaces were immediately visible. High-energy surfaces, such as quartz, were densely populated with droplets, and coalescence proceeded rapidly as the droplets grew into contact with each other. The advancing contact angles of the growing droplets were finite but low (5° to 10°). The receding contact angles were usually 0°, so that retraction did not occur after coalescence. The wetted fraction of the surface thus increased steadily until essentially all of the surface was covered by a film of water. On smooth, low-energy surfaces noticeably fewer droplets formed; however, none of the surfaces were free of nucleation sites. Because of their high advancing contact angles, the growing droplets covered less of the surface area of the insulator than would an equal volume of water in droplets of low contact angle. The leakage current would therefore be expected to be less. More important, however, is the influence of the receding contact angle, which determines the extent of retraction after coalescence of two droplets. This retraction decreases the wetted area of the surface. If the contact angle is 90°, for example, two equal droplets will form one covering an area only 79% of that covered initially. The area uncovered by this retraction is free of bulk water but available again for the initiation of condensation.

As the drops of water on the insulator surfaces increased in size, they reached masses great enough to cause them to leave the positions upon which they had grown and run down the surface, usually accelerating as they swept up droplets in their path. The mobility of a sessile drop depends on the contact angle hysteresis, or the difference between the advancing and receding angles. If the angles are the same, the drop will move freely in response to the slightest force. If there is hysteresis, the force applied to the drop is opposed by a force which is the resultant of the unbalanced interfacial forces. Hysteresis is increased by the absorption of water into the surface under the drop, giving that area greater wettability than the surroundings. Surface roughness can also increase the hysteresis. However, in systems with high contact angles, as the roughness is increased, the advancing contact angle increases and the hysteresis decreases after passing a maximum (20). The water repellency of a surface can therefore be enhanced by roughening it. Plants and animals often take advantage of this effect by covering their surfaces with tiny hairs or other structures of high roughness. A low hysteresis is desirable since this promotes the run-off of condensation, thus reducing the wetted area of the surface and speeding the removal of soluble contaminants from the surface by extraction. For the greatest resistivity in the presence of condensation, an insulator surface should therefore have a low surface energy, should not absorb water, and should either be smooth or very rough. In practice, rough surface coatings are difficult to achieve without compromising adhesion, cohesion, or impermeability. Also, if the roughness falls short of the optimum amount, the increase in hysteresis may more than offset the gain made by the increase in advancing contact angle.

Resistivity of Insulator Surfaces

As condensation formed on the wettable surfaces, their resistivities dropped sharply, often decreasing by a factor of 10^5 or 10^6 in 3 minutes. Less wettable surfaces showed a slower decline in resistivity and did not descend as far. Plots of the changes in resistivity with time for a few representative materials are shown in Fig. 1. Many of the major increases in resistivity were observed to be related to drops of condensate running down the surfaces or dripping off. In addition, there was "noise" (not shown) due to the

Table 1
Surface Resistivity of Insulating Materials During
Exposure to Moisture Condensation

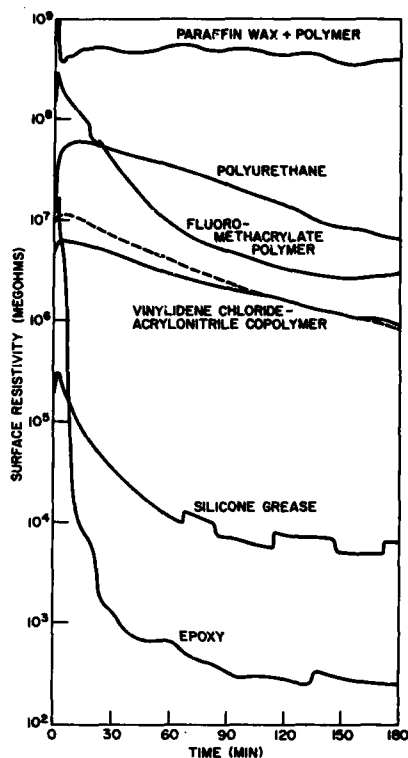| Material	Initial Resistivity (megohms)	Minimum Resistivity (megohms)	Steady-State Resistivity (megohms)	Condensate Contact Angles (degrees)
Poly(tetrafluoroethylene)	$>10^{10}$	—	$>10^{10}$	90-100
Poly(tetrafluoroethylene)	$>10^{10}$	2.7×10^7	$>10^{10}$	—
Poly(tetrafluoroethylene)	10^{10}	10^8	5×10^9	85-105
Polystyrene	5×10^9	$>10^9$	$>10^9$	55-65
Polystyrene	$>10^9$	10^8	$>10^9$	—
Poly(methyl methacrylate)	10^{10}	10^5	6×10^5	40-50
Poly(methyl methacrylate)	10^{10}	8×10^4	2×10^5	50-60
Polyethylene	$>10^9$	6.5×10^3	1.3×10^4	40-50
Polyethylene	$>10^9$	6×10^3	9.5×10^3	40-50
Silicone, glass cloth, rolled (G-7)	7.8×10^8	130	450	30-45
Epoxy, glass filament wound (G-12)	4.5×10^9	80	250	0-35
Epoxy, glass filament wound (G-12)	3.1×10^9	110	150	0-30
Phenolic, nylon cloth, molded, N-1	4.5×10^8	120	200	0-10
Phenolic, nylon cloth, molded, N-1	1.4×10^8	100	200	0-10
Quartz, fused	2×10^5	100	130	0-10
Quartz, fused	4.8×10^5	80	130	0-10
Nylon	4×10^5	65	90	0-20
Nylon	3×10^5	62	90	0-20
Melamine, glass cloth, rolled (G-5)	4.5×10^6	49	55	0-30
Phenolic, paper, molded, XXX	3.8×10^4	17	30	0-15
Phenolic, paper, molded, XXX	7×10^3	15	30	0-15
Phenolic, cotton fabric, molded, LE, Lot 1	2.5×10^5	16	25	0-30
Phenolic, cotton fabric, molded, LE, Lot 1	10^5	10	17	0-10
Lot 2	1.8×10^4	0.85	6	0-5
Lot 3	3.1×10^5	28	80	0-20
	3.2×10^6	32	70	0-10
Lot 4	2.6×10^5	5.4	10	0-10

Fig. 2 - The variation in surface resistivity with time for coatings, on phenolic fabric composite substrates, exposed to moisture condensation (broken line: copolymer with additive)

closely packed monolayers of perfluorinated alkanoic acids. Bernett and Zisman found that polymer A, with a side chain of $-COOCH_2C_7F_{15}$, had a γ_c of 10.6 dynes/cm; polymer S, with a side chain of $-COOC_2H_4N(C_3H_7)-SO_2C_8F_{17}$, had a γ_c of 11.1 dynes/cm. The values for poly(tetrafluoroethylene)(Teflon), polystyrene, and poly(methyl methacrylate) are 18.5, 33, and 39 dynes/cm. In spite of their low critical surface tensions the fluorinated acrylic polymer coatings did not have resistivities as high as these other materials. Pinholes in the coatings were undoubtedly largely responsible, judging from the gradual decline over a long period of time. Also, when the water drops were shaken from the surface after a run, there was little increase in the resistivity. This indicates that the leakage current was flowing through the insulator under the coating rather than on the outer surface of the coating. The lower contact angles measured on the polymer S surface suggest that water absorption by this polymer may be greater, perhaps due to the nitrogen atom and $-SO_2-$ group in the side chain, or to the looser packing of the chains.

The vinylidene chloride acrylonitrile copolymer coating was relatively free of pinholes, but did not have a very low critical surface tension. Jarvis, Fox, and Zisman (22) had reported the reduction of the critical surface tension of polymers by the addition of fluorinated materials capable of adsorbing at the air/solid interface. With 1.33% of bis(1H, 1H-pentadecafluoro-octyl)tetrachlorophthalate added, contact angles about 20° greater were measured, but the increase in resistivity was hardly significant (dashed curve in Fig. 2).

Coatings of refined paraffin wax were quite effective when complete coverage of the surface was attained. This was difficult to accomplish when applying the wax as a solution

Table 2
Surface Resistivity of Coatings During Exposure to Moisture Condensation

Coating	Substrate*	Initial Resistivity (megohms)	Minimum Resistivity (megohms)	Steady-State Resistivity (megohms)	Condensate Contact Angles (degrees)
Silicone resin encapsulant	1	6×10^9	4.5×10^8	1.5×10^9	105-115
Fluorinated vinyl polymer	1	2.1×10^8	2×10^8	10^9	75-80
Silicone resin coating	1	7.8×10^8	10^8	10^9	40-75
Circuit board coating	2	3.5×10^8	10^7	10^9	65-80
Silicone water-repellent treatment	Pyrex glass	10^{10}	8.5×10^8	8.5×10^8	75-90
Paraffin wax with copolymer:					
8:2	1	7×10^8	3.5×10^8	3.5×10^8	90-100
7:3	2	3×10^6	1.0×10^7	1.1×10^7	100-110
7:3	3	1.9×10^5	2.8×10^5	3.1×10^5	100-110
9:1	1	2.1×10^7	1.5×10^3	2.5×10^3	40-80
Polyurethane	1	2.0×10^9	2.4×10^7	2×10^7	55-75
Polyurethane	2	1.1×10^7	6.6×10^6	5×10^6	55-60
Fluorinated acrylate polymer A	3	$>10^9$	5×10^6	$>10^9$	95-105
Fluorinated acrylate polymer A	1	1.6×10^8	2.6×10^6	2×10^6	100-105
Fluorinated acrylate polymer A	2	3×10^7	1.8×10^4	4×10^3	—
Fluorinated acrylate polymer A	2	4.2×10^7	8.5×10^3	4×10^3	100-105
Fluorinated acrylate polymer A	2	1.2×10^7	8.0×10^3	4×10^3	95-105
Fluorinated acrylate polymer S	2	2.0×10^7	1.7×10^3	2×10^3	70-75
Poly(vinyl chloride)	3	1.8×10^5	1.2×10^6	1.5×10^6	60-65
Vinylidene chloride-acrylonitrile copolymer + additive	2	3.7×10^6	8×10^5	5×10^5	65-80
Vinylidene chloride-acrylonitrile copolymer	2	1.8×10^6	9.2×10^5	4×10^5	45-60
Polyurethane	1	3.5×10^8	8×10^5	10^5	55-65
Circuit board coating	2	5×10^6	9×10^4	2×10^4	50-75
Silicone grease	1	1.3×10^5	4.8×10^3	6×10^3	50-60
Epoxy	3	7.6×10^6	4.3×10^3	5×10^3	45-55
Epoxy	2	1.3×10^8	240	250	60-65
Circuit board coating	1	5.2×10^5	180	180	35-50

*1 = Phenolic, cotton fabric, molded, LE, lot 3.
2 = Same, lot 1.
3 = Phenolic, paper, molded, XXX.

in toluene or petroleum ether. The addition of 20 to 30% ethylene-vinyl acetate copolymer (duPont's Elvax) greatly improved the continuity of the coating, preventing the continuing loss of resistivity with time.

A fairly good correlation between the water contact angles and steady-state resistivities for the insulator surfaces can be noted by examining Table 1. The correlation is slightly better for the receding (lower) contact angles. For the coatings in Table 2 the correlation is masked by the effects of volume conductivity under many of the coatings.

Resistivity of Water-Displacing Agents

It was apparent that the application of effective polymer coatings to equipment in the field would be difficult. The surfaces would have to be cleaned and dried, and two coats would have to be applied to ensure that pinholes would not remain. Moving parts and electrical contacts would have to be avoided, or their functioning would be impaired. Heating or prolonged curing or drying were often required. In short, such coatings were suitable only for use during manufacture or overhaul. What the maintenance man needs is a material which he can apply to a rain-soaked terminal strip to restore it to operation, or to a moisture-sensitive circuit board to protect it from the effect of condensation, without the need for disassembly or time-consuming overhaul. Such a material should displace moisture from surfaces, and then dry to a continuous, solid film with a low critical surface tension. The film should be waxy rather than strong or tough, so that moving parts and contacts will be affected as little as possible. The inclusion of a corrosion inhibitor in the formulation would also be desirable, particularly for use on equipment which has been recovered after flooding or fire contamination. A number of water-displacing agents are available from commercial sources, but their effectivenesses in restoring and maintaining insulation resistance were not known. Most of these materials do not dry completely, but leave an oily film on the equipment. Also, most of them displace water by emulsification or preferential wetting. Surface-active additives which aid this process may have adverse effects when the surface is reexposed to moisture.

The protective abilities of five commercial materials were studied under condensing conditions. The resulting data are given in the first section of Table 3, and representative plots are shown in Fig. 3. It can be seen from this figure that these materials offer little or no protection against electrical leakage under these conditions (the performance of the uncoated surface is shown by the dashed line). In the case of material E there was even a considerable adverse effect which diminished as condensation washed the material from the surface. Spra-Dri, or coating B, although an effective water-displacing agent (1-3) which provides a solid film, offered no protection against condensation. The combination of the displacing ability of n-butanol with improved water repellency of the residual film of corrosion inhibitor and other solutes offered an attractive goal.

Development of Improved Displacing Agents

The first step was the development of corrosion inhibitors which would be hydrophobic and resistant to emulsification in bulk form. The amine-acid salts appeared useful for this purpose. Salts prepared from high-molecular-weight acids or anhydrides and long-chain fatty amines often are solid waxy materials capable of providing bulk surface protection as well as adsorbing on metal surfaces as polar corrosion inhibitors. The amine-acid salts were prepared by the combination of stoichiometric quantities of the acid or anhydride and amine in a melt or in solution. A number of compounds having suitable physical properties were applied to phenolic sample surfaces from n-butanol solutions and subjected to condensation. The resistivity and contact angle data for these are given in Table 3, and the data for three of the inhibitors are plotted in Fig. 4. The results were

Table 3
Surface Resistivity of Water-Displacing Agents During Exposure to Moisture Condensation

Code	Coating*	Initial Resistivity (megohms)	Minimum Resistivity (megohms)	Steady-State Resistivity (megohms)	Condensate Contact Angles (degrees)
		Commercial Materials			
A	(Fluid)	5.5×10^5	460	500	15-25
B	Spra-Dri, 3% basic barium dinonylnaphthalene sulfonate in n-butanol	6.8×10^5	41	90	0-30
C	(Fluid)	1.4×10^6	29	60	15-50
D	(Fluid)	3×10^6	2	50	0-25
E	(Fluid)	1.8×10^5	4.8	40	0
E	(Fluid)	1.4×10^4	1	40	0
		Corrosion Inhibitors†			
F	Tetrapropenyl succinic anhydride-arachidyl-behenyl pri. amine	2.2×10^7	150	250	15-60
G	Neutral barium dinonylnaphthalene sulfonate	3.6×10^7	40	150	15-30, emulsion
H	Dimer acid-arachidyl-behenyl propylene diamine	630	30	150	0
I	Dimer acid-arachidyl-behenyl pri. amine	1×10^4	140	110	0 emulsion
J	Dimer acid-arachidyl-behenyl pri. amine	8.7×10^3	110	100	emulsion
K	Dodecylsuccinic anhydride-arachidyl-behenyl pri. amine	1.3×10^3	49	55	30-60
L	Dimer acid-arachidyl-behenyl pri. amine	2.0×10^5	51	30	15-30
M	Cocoyl sarcosine acid-hydrogenated pri. tallow amine	9×10^4	7.3	20	0
N	Dodecylsuccinic anhydride-arachidyl-behenyl propylene diamine	4.8×10^3	19	15	0
		Experimental Formulations‡			
O	Paraffin wax with copolymer and corrosion inhibitor F, two coats	3.4×10^7	1.9×10^7	7×10^7	70-105
O	One coat	4.3×10^7	5.5×10^4	5.5×10^4	65-100
P	Sim. to O, more wax and polymer, Less inhibitor, two coats	3.4×10^7	8.7×10^6	5×10^6	95-105
P	One coat	1.3×10^7	10^7	6×10^5	85-95
Q	Paraffin wax with copolymer and corrosion inhibitor G, with one coat	1.1×10^8	7.2×10^4	3×10^4	75-100
R	Paraffin wax with copolymer and corrosion inhibitor L, one coat	4×10^7	470	900	15-75

*All on phenolic, cotton fabric, molded, LE, lot 3.
†All except G are amine-acid salts. All were applied in two coats from n-butanol except H and L which were applied from 2-propanol.
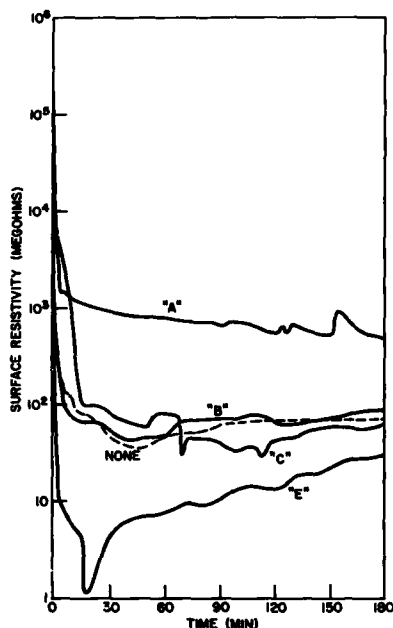‡Dissolved in a mixture of aliphatic naphtha and n-butanol.

Fig. 3 - The variations in surface resistivity with time for several commercial water-displacing agents on phenolic fabric composite, lot 3, exposed to moisture condensation

not greatly different for the various inhibitors, but F, a salt of tetrapropenyl succinic anhydride and arachidyl-behenyl amine, was consistently better in resistivity, resistance to emulsification, and physical properties. This is the same inhibitor which was selected for use in a preservative-lubricant formulation for small arms (23). In that application a slight excess of the anhydride and a light petroleum lubricant were added to obtain different physical properties. An investigation of the reaction mechanism made at that time showed that the anhydride first reacted with the amine to form an amide and a carboxyl group; the latter then reacted with the second equivalent of amine to form an amine-acid salt.

In spite of their waxlike physical properties and resistance to emulsification, the amine-acid salts alone did not offer much protection against electrical leakage. Improvement of this capability was found to require the addition of a wax, polymer, or other hydrophobic coating material. The solubilities of such materials in n-butanol or other suitable water-displacing liquids, however, were generally small. Other solvents, such as aliphatic naphtha, can be mixed with the n-butanol. The water-displacing ability of the mixture is less than that of the alcohol, but it is acceptable over a considerable range of proportions (1,2). Paraffin waxes could be applied from solution, but the coatings were rather porous. The addition of 20 to 30% of an ethylene-vinyl acetate copolymer to the wax permitted the formation of rather effective coatings from toluene solutions, as seen in Table 2. The solution of such a coating material in a butanol mixture, however, is not quite as easy. A number of solvent mixtures were tried, and one with about 58% of 104°F flash aliphatic naphtha and 42% n-butanol was found to be effective as a solvent while also providing water-displacing action.

The solubility of the solids in various solvents was determined by cooling the solution and noting the temperature at which precipitation occurred. The displacing action of the solutions on wet steel panels was observed as previously described. Due to the dilution of the butanol and the greater amount of solids needed for an adequate film thickness, the
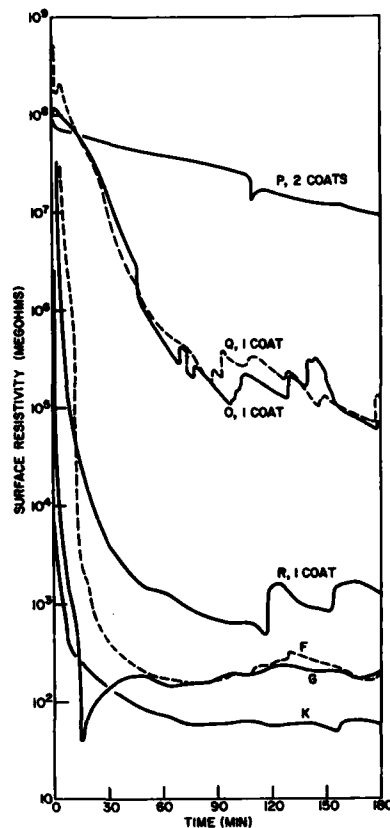
Fig. 4 - The variations in surface resistivity with time for several corrosion inhibitors and experimental water-displacing formulations on phenolic fabric composite, lot 3, exposed to moisture condensation

displacing action of these formulations did not appear to be as vigorous as that of pure butanol formulations with smaller amounts of solute, such as Spra-Dri. Nevertheless, four drops of these solutions typically displaced water from an area 4 to 6 cm in diameter, leaving a continuous water-repellent film. When sprayed from an atomizer onto a vertical wet panel, the displacing action was good but not complete. A number of small immobile droplets remained, leaving holes in the resulting film. The application of a second coat or drying at a temperature above the melting point of the film resulted in complete coverage.

Data on the resistivities of several of these coatings (O, P, Q, and R) are given in Table 3 and Fig. 4. Two coats of O maintained the highest resistivity after prolonged exposure to condensation. It can also be seen that a single coat was only partially effective on porous substrates. Two coats provided 5 to 6 orders of magnitude greater resistivity than the uncoated surface after prolonged exposure.

The complete formulations of these four water-displacing coating solutions are given in Table 4. These solutions were slightly hazy at room temperature and became cloudy at about 10°C. The wax, rather than the polymer, appeared to come out of solution first. This precipitation would prevent application of the material under cold weather conditions. Numerous other solvents were examined, but none was found with a better combination of properties.

Table 4
Experimental Water-Displacing Agent Formulations

Code	O		P		Q		R	
Composition (wt.-%)								
Refined paraffin wax, 124-127°F AMP.*		3.3		3.6		3.6		4.0
Ethylene-vinyl acetate copolymer†		1.2		1.3		1.3		1.0
Corrosion inhibitor‡	(F)	0.8	(F)	0.6	(G)	0.6	(L)	0.5
Oxidation inhibitor**		0.03		0.03		0.03		0.03
Aliphatic naphtha, 104°F flash		54.67		54.47		54.47		54.47
n-Butanol		40.0 / 100		40.0 / 100		40.0 / 100		40.0 / 100
Nonvolatiles (wt.-%)		5.3		5.5		5.5		5.5
Ratio (wax/copolymer)		2.8		2.8		2.8		4.0

*Arco Chemical Co., Division of Atlantic Richfield Company.
†Elvax 250, E.I. duPont de Nemours and Company.
‡(F) 70.6% arachidyl-behenyl primary amine, Kemamine P-190, National Dairy Products Corp.
29.4% tetrapropenyl succinic anhydride, Monsanto Chemical Company.
(G) Neutral barium dinonylnaphthalene sulfonate (solution in low-boiling naphtha),
R. T. Vanderbilt Company.
(L) 52.6% arachidyl-behenyl primary amine, as in (F) 47.4% dimer acid "Empol 1022,"
Emery Industries, Inc.
**2,6-Di-tert-butyl-4-methylphenol.

Effectiveness of Water Displacement

Although the displacement of water from a metal panel was useful as a relative test of water-displacing ability, the effect of various agents on wet insulator surfaces was of greater interest. Sample insulator surfaces were wet with distilled water, and their resistivities were recorded as a water-displacing agent was applied, as previously described. The results are given in Fig. 5. Fabric phenolic samples from lot 3 were used, and the resistivity values have been corrected for variations in the substrate characteristics. Coating O produced the most rapid increase in resistivity until 10 min after application, when it was overtaken by coating B (Spra-Dri). All of the other materials examined were slower by factors of 2 to 5.

The displacing action of formulation O on other substrates was also measured, along with the resistivity of the resulting coating upon exposure to condensation after having been dried, and again after the application of a second coat. These data are given in Table 5. The dry and wet resistivities do not necessarily agree closely with those of Table 1 but are often higher because the "dry" measurements were made at ambient humidity rather than in the test chamber, and the "wet" measurements were made after a much shorter exposure to water than the condensation measurements. It can be seen that the displacement action was effective on a variety of surfaces. Naturally, there was
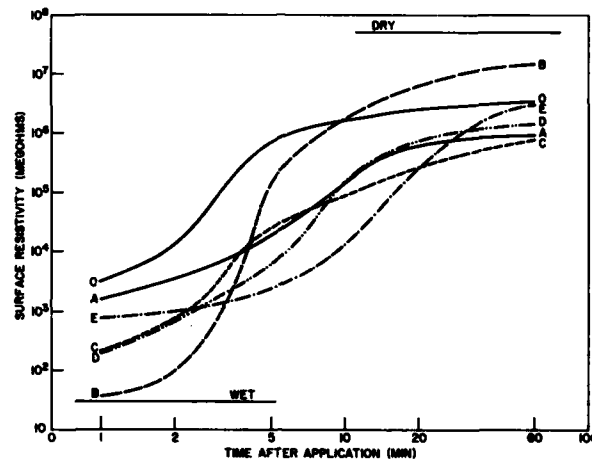
Fig. 5 - The increase in surface resistivity with time during
displacement of water from a phenolic fabric composite
substrate by various water-displacing agents

little or no gain in the use of such a material on a surface which already has a very low
surface energy. The resistivity of the poly(tetrafluoroethylene) was not improved and, in
fact, was lower while the coating was still wet. Upon exposure to condensation, the coat-
ings on nonporous substrates, such as nylon, gave good protection. Coated porous sub-
strates were much better than uncoated ones (compare with steady-state resistivities in
Table 1), but did not approach the maximum attainable values until two coats were
applied. Even then, the most porous, such as the fabric phenolic, did not attain the level
of protection afforded by application to a dry surface (4.7×10^4 compared to 7×10^7
from Table 3). Apparently, water trapped in the pores of these materials prevented com-
plete coverage during displacement, and even the second coat only began to fill them.
Nevertheless, the improvement realized even with these more difficult materials was
significant.

The ability of coating O to protect ferrous metals against corrosion was checked by
spraying one coat on a cleaned panel of cold-rolled steel $3 \times 6 \times 1/32$ in. After the panel
dried for 4 hours, it was immersed in tap water at room temperature. After 23 days of
immersion there were no rust spots on the faces of the panel.

Effect of Coatings on Contacts

As previously noted, the application of a solid, nonconducting film to equipment
having exposed electrical contacts may cause trouble from open circuits and noise. This
is less of a problem on equipment built to military specifications since potentiometers,
relays, and switches are generally enclosed. Nonspecification equipment is occasionally
used and is more likely to cause trouble and require a protection coating treatment. Also,
cable and circuit board connectors and various plugs and sockets are inevitable. The
effects of a few coatings on typical components were evaluated by the technique described
earlier. The cover of the potentiometer was removed so that the contact areas were fully
exposed. While the coatings were drying, the components were placed in the worst orien-
tation, i.e., with the contact areas down so that the coatings ran onto them rather than
draining away before drying. The components were operated while observing the

Table 5
Effect of Coating O in Water Displacement and Subsequent Protection Against Condensation with Various Substrates

Substrate	Surface Resistivity (megohms)				Surface Resistivity Under Condensation (megohms)	
	Dry	Wet	5 Min After Application	60 Min After Application	Initial Coat	Two Coats
Poly(tetrafluoroethylene)	8×10^9	$>10^{10}$	5.7×10^7	2.6×10^9	8×10^9	2×10^9
Epoxy, glass filament wound (G-12)	10^{10}	8×10^3	3.2×10^7	10^9	2.5×10^4	6.3×10^9
Nylon	9×10^8	10^5	3.8×10^7	3×10^8	2.2×10^9	1.1×10^9
Melamine glass cloth, rolled (G-5)	8×10^8	5	1.9×10^4	10^8	3×10^4	4×10^7
Phenolic, paper, molded, XXX	8.2×10^4	18	7×10^4	7.6×10^4	—	4×10^4
Phenolic, cotton fabric, molded, LE, lot 3	5×10^7	30	6.6×10^5	3.4×10^6	320	4.7×10^4

Table 6
The Effect of Coatings on Electrical Contacts

Coating	Number of Operating Cycles to Obtain Noise-Free Contact						
	11-Pin (Round) Connector	Circuit-Board Connector	Wire-Wound Rheostat	4-Pole Lever Switch	12-Pin (Flat) Connector	4-Pole Wafer Switch	Molded Composit. Potentiom.
Spra-Dri, type II	—	—	0	—	—	—	0
Silicone grease	—	—	0	—	—	—	0
Fluid A	—	—	1	0	—	—	1
B, Spra-Dri, type I	—	—	5	—	—	0	4
B, Spra-Dri, type I	0	0	3	5	0	3	9
O, one coat	1	1	3	5	25	14	26
O, two coats	1	8	8	5	10	28	30
Silicone resin coating	—	—	>40	—	—	9	>40

oscilloscope for indications of open circuits or noise. If any was detected, operation was continued until the film was worn through and the component operated reliably and without noise.

In Table 6 the numbers of operating cycles to reach the noise-free condition are given for several coatings on the various components. The fluid coatings and those with very low nonvolatile contents caused little noise. (Spra-Dri, type I, contains 3.25% nonvolatiles; type II has 0.75%.) The silicone coating, although waxy, was thicker and therefore took longer to wear through in most cases. Coating O gave some trouble, but eventually wore off of all contacts. The application of this coating to contact areas should be minimized to reduce the possibility of contact noise. It can also be wiped off while wet, or washed off with a solvent, such as toluene or many contact cleaners. After the coating has dried, any affected components should be operated a few times to ensure good contact. On many moving parts the waxy film will improve operation by serving as a dry-film lubricant.

CONCLUSIONS

The desirability of using insulating materials and protective coatings with low critical surface tensions of wetting (low surface energies) in equipment exposed to moisture condensation has been reaffirmed. Under conditions of continuous condensation, the surface resistivity of such a material can be 8 or 9 powers of ten higher than that of a porous, hydrophilic material because the moisture is in the form of drops with large contact angles rather than a continuous film. The fluorocarbon, hydrocarbon, and silicone coatings have low surface energies, but their potentially high resistivities may not be attained if they are porous or absorb moisture.

Most water-displacing agents offer little protection against subsequent reexposure to moisture. Those which contain a nonvolatile oil and surface-active material to aid the emulsification of water may cause the surface resistivity to fall below that of an untreated surface.

A material (formulation O of Table 4) has been developed which combines the effective water-displacing action of butyl alcohol, a corrosion-inhibiting film for metal parts, a dry-film lubricant for moving parts, and a highly water-repellent dry film which greatly reduces the surface conductivity of insulation exposed to moisture and condensation. On porous materials a single coat maintained the resistivity under conditions of moisture condensation higher by a factor of 10^3 than on uncoated equivalents. Two coats offered an improvement of 10^6. On less porous substrates improvements of 10^4 and 10^7, respectively, were observed. After 3 hours of continuous condensation, the coating was found to maintain a surface resistivity as high as 6×10^9 megohms.

When the resistivities of insulator surfaces were monitored during the displacement of water by various agents, this solution increased the resistivity 2 to 5 times as rapidly as all others examined, except for the butanol solution Spra-Dri, which surpassed it after 10 minutes. The resistivity of a wet porous insulator surface was increased by a factor of 2×10^4 in 5 minutes.

Application of the coating to switch and variable resistor contacts should be avoided. However, all of the typical components on which the coating was evaluated cleaned themselves as they were operated and became free of noise.

This moisture-displacing and coating solution would be beneficial to those portions of aircraft and missile electrical and electronic equipment which are exposed to the environment. It would be an aid in the maintenance of shipboard fire control and communications circuits, power circuits, and automotive equipment, such as aircraft engine starters, which are exposed to moisture and salt aerosols. (Heavily contaminated equipment should be cleaned first for best results.) In cases of accidental flooding of vital equipment or wetting

by sea spray or by fire fighting, the wet equipment could be rapidly restored to operation by flushing it with fresh water and applying the displacing solution. Corrosion would be inhibited, and deterioration of the equipment pending a thorough cleaning would be prevented. After cleaning and rinsing (3-7) or following accidental fresh-water flooding, this solution could be applied to dry the insulation and give it protection against electrical leakage.

It is recommended that this material be evaluated in field tests to determine its suitability and effectiveness on various types of equipment under typical and severe operating conditions.

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